

Reverse Monte Carlo modeling of amorphous siliconParthapratim Biswas,* Raymond Atta-Fynn,[†] and D. A. Drabold[‡]*Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701, USA*

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An implementation of the reverse Monte Carlo algorithm is presented for the study of amorphous tetrahedral semiconductors. By taking into account a number of constraints that describe the tetrahedral bonding geometry along with the radial distribution function, we construct a model of amorphous silicon using the reverse Monte Carlo technique. Starting from a completely random configuration, we generate a model of amorphous silicon containing 500 atoms closely reproducing the experimental static structure factor and bond angle distribution and in improved agreement with electronic properties. Comparison is made to existing reverse Monte Carlo models, and the importance of suitable constraints beside experimental data is stressed.

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I. INTRODUCTION

The structure of amorphous semiconductors is well represented by continuous random network (CRN) model introduced by Zachariassen¹ 70 years ago. The CRN model has the simplicity that each of the atoms should satisfy its local bonding requirements and should have as small strain as possible in the network, which is generally characterized by having a narrow bond angle as well as bond-length distribution. In spite of its apparent simplicity, the structural modeling of high quality tetrahedral amorphous semiconductors appears to be quite difficult. There have been many models of amorphous silicon^{2–11} proposed in the last 30 years which include from very simple hand-built model of Polk,² computer generated periodic network model of Guttman³ to the complex model of Wooten, Winer, and Weaire (WWW),⁴ but most of these models have some limitations in one way or another in describing the true nature of the amorphous state. The last method, the so-called *sillium* approach of WWW, based on the strategy of randomizing and relaxing the network, is so far the most successful method of producing minimally strained CRN. The algorithm, in its modified form developed by Djordjević *et al.*⁷ and Barkema and Mousseau,⁵ can produce a CRN that is comparable to experimental results and is capable of producing a clean band gap without any defect states in the gap.

In this paper we develop a different approach to model amorphous semiconductors known as reverse Monte Carlo (RMC) simulation.^{12–18} Our primary objective is to produce structural configurations that are consistent with experimental data but at the same time we go one step further to generate realistic configurations for comparison with models obtained via other routes. We emphasize that producing realistic models (meaning models which agree with all experiments) requires more than spatial pair correlations, and identify additional constraints which lead to realistic models.

The existing RMC models of amorphous semiconductors are found to be inadequate and fail to produce some of the basic experimental features of amorphous tetrahedral semiconductors. Gereben and Pusztai^{12,13} have carried out RMC simulation of tetrahedral semiconductors using a number of models ranging from completely disordered configuration to randomized diamond structure. Although a certain degree of

tetrahedral character in the bond angle distribution was reflected in their work, most of the models show an unphysical peak in bond angle distribution around 60°. ¹⁹ The work of Walters and Newport¹⁴ on amorphous germanium made some progress toward getting the correct bond angle distribution, but the number of threefold coordinated atoms is quite high in their model, and in the absence of any discussion on local strain and electronic properties it is difficult to say how reliable their models are when it comes looking at the electronic properties.

A developing area where RMC may be applied successfully is for modeling amorphous materials exhibiting medium-range order (MRO). Such MRO is characterized by the existence of 10–20 Å scale structure. Recent developments in fluctuation electron microscopy (FEM) (Ref. 20) and its application on amorphous germanium and silicon have indicated that computer generated CRN model of these materials lacks the characteristic signature of MRO. Since RMC is based on experimental data, it provides a promising scheme to model amorphous materials having medium-range order by including the experimentally measured FEM signal as input data to augment pair correlations.

The plan of the paper is as follows. In Sec. II, we briefly mention the basic philosophy of reverse Monte Carlo modeling and some of its salient features. This is followed by role of constraints in RMC modeling in Sec. III where we illustrate how a set of judiciously chosen constraints can be used to construct a reliable model of amorphous silicon. Finally we compare our results with those obtained from earlier RMC models, models obtained via WWW algorithm and experimental structure factor.

II. BASICS OF RMC

The RMC method has been described in detail elsewhere.¹⁵ Here we briefly outline the basic philosophy of RMC. At the very basic level, RMC is a technique for generating structural configurations based on experimental data. The logic is very appealing: any model of a complex material worthy of further study should, at a minimum, agree with what is known (that is, the experiments). By construction, the RMC scheme enforces this (and for contrast, a molecular-dynamics simulation may not). In an ideal imple-

mentation, one should find a model agreeing with *all* known information, but this is not easy to accomplish, though we make some progress below. The approach was originally developed by McGreevy & Pusztai^{15,12} for liquid and glassy materials for lack of different routes to explore experimental data, but in recent years progress has been made toward modeling crystalline systems as well.²¹ Starting with a suitable configuration, atoms are displaced randomly using the periodic boundary condition until the input experimental data (either the structure factor or the radial distribution function) match with the data obtained from the generated configuration. This is achieved by minimizing a cost function which consists of either structure factor or radial distribution function along with some appropriately chosen constraints to restrict the search space. Consider a system having N atoms with periodic boundary condition. One can construct a generalized cost function for an arbitrary configuration by writing

$$\xi = \sum_{j=1}^K \sum_{i=1}^{M_j} \eta_i^j \{F_E^j(Q_i) - F_c^j(Q_i)\}^2 + \sum_{l=1}^L \lambda_l P_l, \quad (1)$$

where K is the total number of different experimental data set, M_j is the total number of data points for data set j , and L is the total number of constraints. η_i^j is related to the uncertainty associated with the determination of data points as well as the relative weight factor for each set of different experimental data. The quantity Q is the appropriate generalized variable associated with experimental data $F(Q)$ and P_l is the penalty function associated with each constraint. For example, in case of radial distribution function and structure factor, Q has the dimension of length and inverse length, respectively. In order to avoid the atoms getting too close to each other, a certain cutoff distance is also imposed which is typically of the order of interatomic spacing. In RMC modeling, this is usually obtained from the radial distribution function by Fourier transform of the measured structure factor. This is equivalent to adding a hard-sphere potential cutoff in the system which prevents the catastrophic buildup of potential energy.

In spite of the fact that RMC has been applied to many different types of systems—liquid, glasses, polymer, and magnetic materials, questions are often raised about the reliability of results obtained from RMC simulation. The method has never been accepted without some degree of controversy, and the most popular criticism is the lack of unique solution from RMC. RMC can produce multiple configurations having the same pair correlation function. This lack of uniqueness, however, is not surprising, since usually only the pair correlation function or structure factor is used in modeling the structure, while there exists an infinite hierarchy of higher-order correlation functions carrying independent structural information are neglected. In other words, RMC samples from the space of all models consistent with some limited body of data—in its simplest form (analyzing a single experiment) RMC is an ideal gauge of how *nonspecific* the data is with respect to identification of an atomistic model. If the modeler possesses *a priori* information independent of that implicit in the experiment being fit to, it is

necessary to add this information to the modeling in some fashion to receive a model in joint agreement with the experiment and the additional information.

III. A RMC MODEL

We begin by including the minimal information that is necessary to model a configuration of *a*-Si. In doing so, we use the radial distribution function (RDF) obtained from a high quality model of amorphous silicon. This latter model was generated by Barkema and Mousseau⁵ using a modified form of WWW algorithm⁴ having bond angle distribution close to 10° with 100% fourfold coordination. In addition to this RDF, we also impose the conditions that the average bond angle of all the triplets Si-Si-Si should be near 109.5° and the corresponding root-mean-square deviation should be equal to or less than 10° . The number of fourfold coordinated atoms is driven to a specified value during the simulation by including a constraint on the average coordination number. It is to be noted that while there is no limit to the number of constraints that can be included in the system, there is no guarantee that mere inclusion of more constraints will necessarily give better results. Forcing a completely random configuration with too many competing constraints may cause the configuration to be trapped in the local minimum of the function ξ and may prevent the system from exploring a large part of the search space. By adding only the essential constraints that describe the chemical and geometrical nature of the bonding correctly, Eq. (1) can be written as

$$\xi = \sum_{i=1}^M \lambda_1 \{F_E(x_i) - F_c(x_i)\}^2 + \lambda_2 (\theta_0 - \theta)^2 + \lambda_3 (\delta\theta_0 - \delta\theta)^2 + \lambda_4 \{1 - \Theta(x - x_c)\} + \lambda_5 \{\phi_0 - \phi\}^2, \quad (2)$$

where

$$\theta = \frac{1}{N_\theta} \sum_{i\{j,k\}} \theta_{ijk},$$

$$\delta\theta = \sqrt{\langle (\theta - \theta_0)^2 \rangle},$$

In Eq. (2), θ and $\delta\theta$ are the average angle and the rms deviation while ϕ and ϕ_0 are the current and proposed concentration of the fourfold coordinated atoms. It is important to note that each of the terms in Eq. (2) is non-negative, and should decrease ideally to zero during the course of minimization. Since the cost of energy associated with the bond-length relaxation is more than the bond angle relaxation, atomic arrangements with broad bond angle distribution but having correct RDF frequently result. The coefficients, λ_1 to λ_3 , for the different terms in Eq. (2) can be chosen appropriately to minimize this effect. In general the coefficients λ are constant during the course of simulation but the minimization procedure can be slightly accelerated by making them vary in such a way that the contribution from each of the terms is of the same order during the course of simulation. The coefficient λ_4 is usually assigned a large value in order to include a hard-sphere cutoff as mentioned earlier, so that no two particles can come closer to x_c while the coefficient

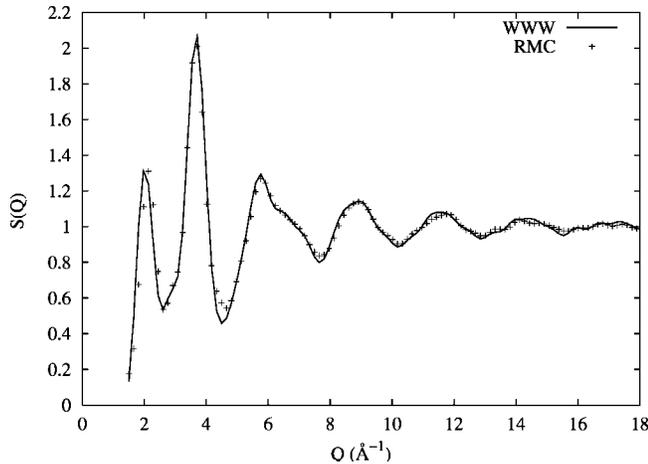


FIG. 1. Structure factor obtained from a RMC model containing 500 atoms of a -Si. The solid line is obtained from a WWW sample of identical size and number density of atoms.

λ_5 maintains the number of fourfold coordinated atoms to a specified value. In RMC simulation of amorphous tetrahedral semiconductors one usually encounters the problem of having a pronounced peak at 60° . This peak is a characteristic feature of unconstrained RMC simulation and is due to the formation of equilateral triangles by three atoms. In the work of Gereben and Pusztai,^{12,13} attempts were made to overcome this difficulty by constraining the bond angle distribution as well as by making an initial configuration which is 100% fourfold obtained from a diamond lattice. The resulting structure is, however, found to be unstable and on relaxation using a suitable potential, the configuration tends to get back toward the starting structure, i.e., randomized diamond in this case.²² In the approach of Walter and Newport,¹⁴ the initial random configuration was examined and any “triples,” i.e., three atoms forming an equilateral triangle, were removed before the beginning of RMC fit. By selective removal of such unwanted triplets, they have been able to generate configuration of a -Ge without having a peak at 60° . The approach that we have taken in our work is more general and starts with a completely random configuration. This eliminates, in the first place, any possible local ordering that may exist in the starting structure (e.g., randomized diamond structure retains the memory of tetrahedral ordering). Furthermore, we have not included or excluded any special configuration in our starting structure, e.g., three atoms forming an equilateral triangle. Based on experimental consideration, we have included only the key features of amorphous tetrahedral semiconductors—an average bond angle of 109.5° having rms deviation of 10° which is consistent with the RDF obtained from a WWW relaxed model used in our calculation. For the 500-atom model reported in this work, we have chosen a cubic box of length 21.18 \AA that corresponds to number density $0.0526 \text{ atom/\AA}^3$. The initial configuration is generated randomly so that no two atoms can come closer to 2.0 \AA . The configuration is then relaxed by moving the atoms to minimize the cost function ξ . In addition to applying standard Monte Carlo moves in which a single or a group of atoms is randomly displaced, a variety of Monte Carlo

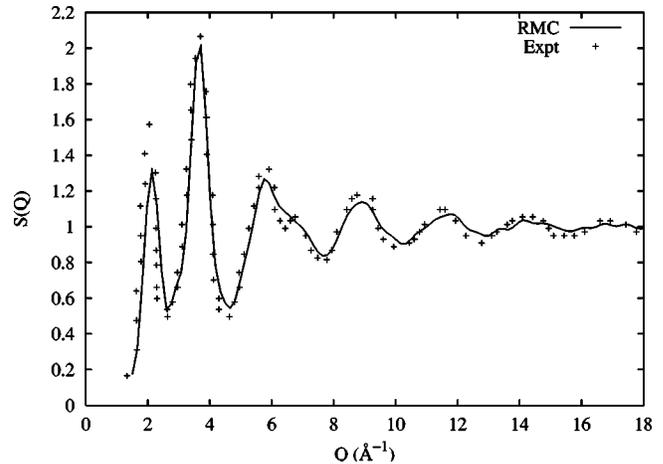


FIG. 2. Structure factor obtained for a 500-atom model of a -Si from RMC (solid line) and the experiment of Laaziri *et al.* as indicated in the figure.

moves have been implemented in our work. For example, in one such moves, a threefold or fivefold atom is selected and the nearest-neighbor distance is examined. If the distance is greater than 2.7 \AA , the neighboring atom is displaced in order to bring the distance within a radius of 2.7 \AA . The maximum displacement of a Monte Carlo move is limited to $0.2\text{--}0.4 \text{ \AA}$ throughout the simulation. Since we are interested in the electronic structure as well, we confine ourselves within a reasonable system size for studying the generated structure using a first-principles density-functional Hamiltonian. The density-functional calculations were performed within the local density approximation (LDA) using the local basis first-principles code SIESTA.²³ We have used a non-self-consistent version of density-functional theory based on the linearization of the Kohn-Sham equation by Harris functional approximation²⁴ along with the parametrization of Perdew and Zunger²⁵ for the exchange-correlation functional.

IV. RESULTS

The results for the model including all the constraints are presented in Figs. 1–4. Since the structure factor is generally considered to be more sensitive to an arbitrary small change in the atomic positions than the radial distribution function, we have plotted the structure factors for the constrained RMC and WWW models in Fig. 1. It is evident from Fig. 1 that the agreement between the RMC and WWW models is very good both for small and large values of Q . In order to further justify the credibility of our model, we have plotted in Fig. 2 the structure factor from the experiment of Laaziri *et al.*²⁶ along with the same obtained from our RMC model. Once again we find that the agreement between the structure factor from RMC and the experimental results is quite good except for the few points near the first peak. It is very tempting to think of this deviation as a finite-size effect coming from the finiteness of our model. We have therefore calculated the structure factor for WWW models containing 300 to 4096 atoms of Si, but the deviation continues to remain. Holender and Morgan¹¹ also observed similar deviation near

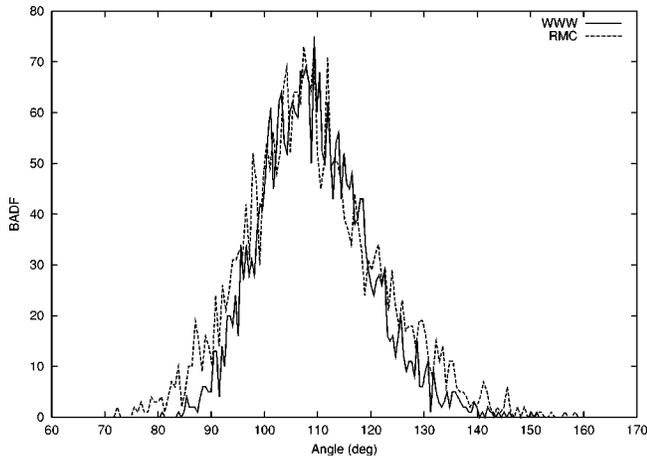


FIG. 3. The bond angle distribution functions (BADF) for 500-atom model of *a*-Si from constrained RMC (dashed line) and WWW model (solid line). The rms deviations for the models are 12.5° and 9.9° , respectively.

the first peak in their work with a much larger model containing 13 824 atoms which was compared with the experimental data obtained by Fortner and Lannin.²⁷

In Fig. 3, we have plotted the bond angle distributions (BADF) for both the RMC and WWW model. As we have discussed in Sec. II, the radial distribution function or structure factor cannot alone provide all the necessary information that is needed to characterize an atomic configuration obtained from a reverse Monte Carlo simulation. A further characterization beyond pair correlation function is therefore vital and necessitates the need for getting some idea about the three-body correlation function. It is clear from Fig. 3 that the distribution obtained from the RMC model follows the tetrahedral character observed in amorphous semiconductors. The average bond angle in this case is found to be 109.01° with rms deviation of 12.5° . An important aspect of the bond angle distribution in Fig. 3 is that most of the angles are lying between 70° – 150° compared to 80° – 140° in WWW case. We emphasize at this point that the earlier

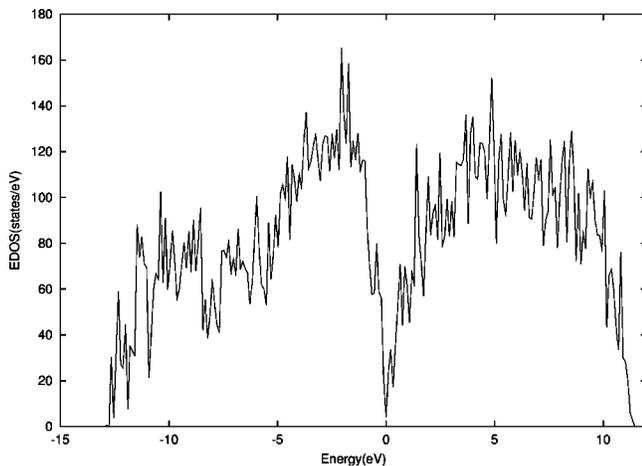


FIG. 4. The electronic density of states (EDOS) of 500-atom model of *a*-Si obtained from RMC simulation described in the text. The Fermi level is at $E=0$.

works on modeling amorphous tetrahedral semiconductors using RMC predicted a much wider bond angle distributions. Gereben and Pusztai¹² have observed a pronounced, unphysical peak at 60° except for the model starting with diamond structure, while Walters and Newport¹⁴ have reported a bond angle distribution of *a*-Ge that is as wide as 60° – 180° . It is an important development here that by adding three more constraints (λ_2, λ_3 , and λ_4) we have achieved significantly improved results. Both the radial and the bond angle distribution functions reported here are at par with the results obtained from molecular-dynamics simulation and are comparable to those obtained from WWW model. The fact that the inclusion of these two constraints leads to a significant improvement is not surprising. For a large CRN model of amorphous tetrahedral semiconductor, one can approximate the bond angle distribution as nearly Gaussian.²⁸ This approximated Gaussian distribution can be defined by the first two moments of the distribution function. By specifying these two moments as constraints in Eq. (2), we correctly describe the tetrahedral bonding geometry of the atoms, which along with the radial distribution function produces a configuration more realistic than those obtained from models based on RDF or structure factor only. This suggests that in addition to the radial distribution of the atoms, one needs to include some relevant information about the nature of three-body correlation among the atoms to construct a realistic configuration.

Having studied the radial and bond angle distribution we now address the electronic density of states calculations. While the width of the BADF and the structure factor together indeed gives some idea about the quality of the model, some of the features, e.g., the existence of spectral gaps and the position of defect states in the spectrum, can be studied by looking at the electronic density of states only. The structure obtained from RMC simulation is first relaxed using the density-functional code SIESTA and is found to be close to an energy minimum in the LDA. This is an important test for determining the stability of the structure obtained from RMC simulation, and as far as we are concerned almost all earlier works on RMC have completely neglected this issue. In Fig. 4, we have plotted the electronic density of states (EDOS) for the constrained model. The EDOS appears with all the characteristic features of *a*-Si with the exception of a clean gap in the spectrum. This behavior is not unexpected in view of the fact that 88% of the total atoms are found to be four-fold coordinated with an average coordination number 3.85. The presence of the defect states makes the gap noisy and at the same time the use of LDA underestimates the size of the gap. This EDOS is in significantly better agreement with optical measurements than conventional RMC models with much higher defect concentrations and spurious bond angles. It is interesting to observe that the average coordination number from our model is very close to the experimental value of 3.88 reported by Laaziri *et al.*²⁶

V. CONCLUSIONS

We have presented a model of amorphous silicon based on reverse Monte Carlo simulation. One of the features of

our model is to start with a completely random structure and then to relax toward a realistic configuration by adding a number of physically relevant constraints. The characteristic features of the tetrahedral bonding are taken into account by adding constraints on average bond angle and its deviation from the mean, while the number of fourfold coordinated atoms is maintained at a specified value by further use of a constraint on average coordination number. The radial and the bond angle distribution obtained from our model is found to be in excellent agreement with a high quality CRN model produced by WWW algorithm. We have also compared the structure factor with the experimental data obtained by Laaziri *et al.* and observed a reasonably good agreement. By relaxing the model using the first-principles density-function code SIESTA, we find that the model is close to the energy minimum for LDA and is stable. The electronic density of states (EDOS) obtained from our model contains all the essential feature of amorphous silicon including a signature of the band gap. Although the model does not produce a clean gap in the spectrum, the quality of the EDOS is at par with

models obtained from molecular-dynamics simulation. Our RMC algorithm presents a significant improvement on previous RMC studies and makes it possible to compare, albeit qualitatively, the structural and electronic properties of RMC models with its WWW counterpart. We expect that further developments toward this direction will eventually make RMC a useful modeling tool incorporating experimental information and it can be used effectively without any criticisms in modeling complex materials.

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